



Enhanced electroreduction of CO₂ and simultaneous degradation of organic pollutants using a Sn-based carbon nanotubes/carbon black hybrid gas diffusion cathode

Qinian Wang^{a,b,*}, Xinqi Wang^{a,b}, Chao Wu^{a,**}, Yuanyuan Cheng^c, Qingye Sun^a, Hongbing Yu^d

^a College of Resources and Environmental Engineering, Anhui University, Hefei, Anhui, 230601, China

^b Mining Environmental Restoration and Wetland Ecological Security Collaborative Innovation Center, Hefei, Anhui, 230601, China

^c School of Life Sciences, Anhui University, Hefei, Anhui, 230601, China

^d College of Environmental Science and Engineering, Nankai University, Tianjin 300071, China

ARTICLE INFO

Keywords:

Carbon dioxide
Electroreduction
Gas diffusion electrode
Formic acid
Electrochemical system

ABSTRACT

Coupled electrochemical system (CES) for electroreduction of CO₂ and simultaneous degradation of organic pollutants is a promising CO₂ conversion method. However, its performance is severely restrained by insufficient reactants and low electroactive surface areas on the cathode material. Here, a series of novel Sn-based carbon nanotubes (CNTs)/carbon black hybrid gas diffusion electrodes (CNTx/ESGDEs) were fabricated and used as cathodes to enhance the performance of the CES with methyl orange (MO) as a target pollutant. The results show that at an appropriate content of CNTs, the CNTx/ESGDEs offered increased total pore area, porosity, electroactive surface area, and decreased charge transfer resistances. The current density, Faraday efficiency, formic acid production rate, MO removal efficiency, and COD removal efficiency were improved by 140%, 92%, 404%, 76%, and 131%, respectively, at 40 wt% CNTs probably due to enhancement in the electroactive surface area as well as reactant transfer. This study benefits the large-scale applications of CES.

1. Introduction

The carbon dioxide (CO₂) concentration in the atmosphere has continuously increased and recently reached 400 ppm. Continuous increases in CO₂ concentration are expected to lead to undesirable climate effects [1–3]. Therefore, it is critical to curb these future increases in atmospheric CO₂ [1–3]. Electroreduction of CO₂ offers a promising solution to this problem. CO₂ can be converted into useful chemicals and fuels after electroreduction including formic acid, carbon monoxide, and hydrocarbons [3–7]. Formic acid is an additive widely used in the field of textile, leather and dye industries. It is also a promising hydrogen storage medium [8]. The electroreduction of CO₂ to formic acid (ERCF) process is also suitable for large-scale production [8–11].

In most ERCF systems, the CO₂ reduction reaction ($\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$) occurs on the cathode while the water oxidation reaction ($\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$) occurs on the anode [11–14]. Oxygen (O₂) formed on the anode is a low-value gas [15]. A more beneficial electrochemical reaction on the anode would improve the feasibility of the ERCF process for large-scale applications. However, few attempts have been made in this regard [16]. Recently, some

researchers developed a coupled electrochemical system (CES) for simultaneous ERCF and treatment of organic pollutants (i.e. using electrooxidation of organic pollutants as a substitute for water oxidation on the anode) [17–19]. This CES substantially improves the feasibility of the ERCF process in industrial applications [19].

The cathode materials play an important role in CES. An ideal cathode material should possess excellent electrochemical performance (e.g. Faraday efficiency, production rate) [16], sufficient reactants (e.g. CO₂, electron), a large electroactive surface area as well as excellent electrocatalytic activity of the associated catalysts on the cathode material [2,16]. Currently, the cathodes utilized in CES are solid electrodes with Sn catalysts. Although Sn is a state-of-the-art non-noble metal catalyst for ERCF [20–24], the very limited CO₂ solubility in the electrolyte (ca. 0.033 M) and low electroactive surface area definitely lead to low electrochemical performance [25–27]. Thus, it is necessary to exploit a new cathode material to solve these problems for industrial applications of CES.

Gas diffusion electrodes (GDE) are porous composite electrodes that usually consist of a catalyst layer (CL) and a gas diffusion layer (GDL) [28–30]. The GDL can transport gas, prevent water leakage, and reduce

* Corresponding author at: College of Resources and Environmental Engineering, Anhui University, Hefei, Anhui, 230601, China.

** Corresponding author.

E-mail addresses: wqn88@126.com (Q. Wang), benny928@mail.ustc.edu.cn (C. Wu).

Ohmic losses. The CL is porous and has a gas-liquid-solid three-phase interface that is the reaction site [31]. The traditional method for preparing a GDE is to spray a catalyst ink including Nafion binder and catalyst (e.g. Sn particles, Cu₂O particles, metal-organic porous materials) onto a GDL (e.g. carbon paper) [16,25,32,33]. Versus a solid electrode, the GDE improves CO₂ transport and presents a larger electroactive surface area [28,34,35]. However, the electron transfer barriers within the CL and between the CL and GDL restrain the availability of the electroactive surface area, resulting from the non-conductivity of Nafion binder [32,34].

In our previous work, a novel GDE (ESGDE) was developed via the electrodeposition of an Sn catalyst on the CL of Nafion-bonded carbon black (CB). This enhanced the electroactive surface area and increased reactant transfer [32]. Here, to acquire better electron transfer efficiency and larger electroactive surface areas, carbon nanotubes (CNTs) were added into the CL of the ESGDE named CNTx/ESGDEs where x indicates the mass percent (wt%) of CNTs in the composite of CB and CNTs. Subsequently, the as-prepared CNTx/ESGDEs were used as cathodes in the CES for ERCF. They simultaneously degraded the organic pollutant methyl orange (MO). To the best of our knowledge, GDE has not yet been used in the CES for ERCF and simultaneous degradation of organic pollutants. Composite carbon materials have not been used in the CL of the GDE for ERCF.

2. Experimental

2.1. Materials

CB was obtained from Cabot Corporation, and CNTs (8–15 nm diameters) were obtained from Tanfeng Co. Ltd. The polytetrafluoroethylene (PTFE, 60 wt%) was obtained from Hesen Co. Ltd., and Nafion ionomer (5 wt%) was obtained from DuPont Corporation. The KHCO₃, SnCl₂, and other chemicals were of analytical grade and purchased from Sinopharm Chemical Reagent Co. Ltd. Milli-Q water was used to prepare aqueous solutions.

2.2. Fabrication of the CNTx/ESGDEs

The CNTx/ESGDE consists of a GDL and a CL. The GDL was made of CB, PTFE, and brass mesh (30 mesh) via a roll-pressed method according to a procedure described previously [32]. To prepare the CL, a mixture of CB and CNTs with different mass ratios was first individually dispersed into a mixture solution of Nafion ionomer, isopropyl alcohol, and deionized water to form an ink followed by spraying this ink onto the GDL as a CL support. The weight ratio of CB + CNTs, Nafion ionomer, isopropyl alcohol, and deionized water was 1:1:20:20. The total amount of CB and CNTs in each CL support was 1 mg cm⁻². Finally, Sn was electrodeposited on each CL support in 0.05 M SnCl₂ solution with a potential of -2 V vs. Ag/AgCl and a charge of 20 C. The ESGDE was similarly prepared as control.

2.3. Physical characterization

The surface morphologies of Sn catalysts in the ESGDE and CNTx/ESGDEs were examined by scanning electron microscopy (SEM, S-4800, Japan) and transmission electron microscopy (TEM, JEOL-2100, Japan). The size of the Sn catalysts in TEM images was analyzed using Nano Measurer 1.2 software that is based on pixel counting as described previously [36]. The total pore area and porosity of the ESGDE and CNTx/ESGDEs were measured with a mercury porosimeter (AutoPore Iv 9510, Micromeritics, USA). The crystal structures of the Sn catalysts in the ESGDE and CNTx/ESGDE were investigated by X-ray diffraction (XRD, Smart Lab 9KW, Japan) with Cu-Kα radiation. The surface elemental compositions of the ESGDE and CNTx/ESGDE were investigated by X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Fisher Scientific Inc., USA) operating at 10⁹ Pa with Al Kα radiation (1486.6 eV).

2.4. Electrochemical measurements

The electrochemical measurements for the as-prepared ESGDE and CNTx/ESGDEs were carried out in a three-electrode electrochemical cell with an electrochemical workstation (CHI600E, Shanghai Chenhua, China). The ESGDE and CNTx/ESGDEs (3.14 cm²), platinum wire, and Ag/AgCl (saturated KCl) electrode were used as the working electrode, counter electrode, and reference electrode, respectively.

Linear sweep voltammetry (LSV) experiments were tested at a scan rate of 50 mV s⁻¹ from 0 to -1.6 V vs. Ag/AgCl. Electrochemical impedance spectroscopy (EIS) measurements were performed from 100 kHz to 0.1 Hz. Before each measurement, N₂ was bubbled into the electrolyte (0.5 M KHCO₃ solution) for at least 30 min. During the measurements, N₂ or CO₂ was continuously fed to the working electrode at a flow rate of 10 mL min⁻¹.

2.5. ERCF and simultaneous degradation of MO tests

The ERCF and simultaneous degradation of MO used an electrochemical cell shown in Fig. S1. The anode chamber and the cathode chamber were separated by a proton exchange membrane (PEM, Nafion 117, Dupont, USA). The ESGDE and CNTx/ESGDEs (3.14 cm²) served as cathodes. An Ag/AgCl (saturated KCl) electrode was used as the reference electrode (RE), and a Co₃O₄-coated graphite electrode with a geometric surface area of 3.14 cm² (Co₃O₄ loading: 2 mg cm⁻²) was used as the anode. The spacing of the cathode and the anode was held at 4 cm.

Testing of ERCF and simultaneous degradation of MO were done under a constant cathode potential via an electrochemical workstation (CHI600E, Shanghai Chenhua, China). The catholyte was 0.5 M KHCO₃, and the anolyte was 0.5 M KHCO₃ solution consisting of MO of 10 mg L⁻¹. The electrolysis time was 30 min—the CO₂ was directly fed to the cathode throughout the electrolysis at a flow rate of 10 mL min⁻¹.

The gaseous products were analyzed with gas chromatograph (GC, Agilent 7890 A, USA). The concentration of formic acid in the catholyte was analyzed with an ion chromatography (ICS-1500, Dionex, USA) at a flow rate of 1 mL min⁻¹. The Faraday efficiency (f_{HCOOH}) of the formic acid was calculated according to Eq. (1) as follows:

$$f_{\text{HCOOH}} = \frac{2 \times n_{\text{HCOOH}} \times F}{Q} \quad (1)$$

Here, 2 is the number of electrons needed to produce formic acid from CO₂; n_{HCOOH} represents the moles of produced formic acid (mol); F is Faraday's constant (96,485 C mol⁻¹); and Q is the total charge passed during the electrolysis process (C).

The MO concentration in the anolyte was analyzed with a spectrophotometer (UV-1100, Meipuda Instruments Equipment Co. Ltd., China) at 464 nm. The chemical oxygen demand (COD) of the anolyte samples were measured with a standard method. The removal efficiency of MO was calculated according to Eq. (2) as follows:

$$\text{MO removal efficiency} = \frac{C_0 - C_t}{C_0} \quad (2)$$

where C_0 and C_t represent the MO concentration before electrolysis and after an electrolysis time t , respectively.

The COD removal efficiency was calculated according to Eq. (3) as follows:

$$\text{COD removal efficiency} = \frac{\text{COD}_0 - \text{COD}_t}{\text{COD}_0} \quad (3)$$

where COD_0 and COD_t represent the value before electrolysis and after an electrolysis time t , respectively.

The current density (J) is expressed as the current divided by the geometric area of the cathode.

Download English Version:

<https://daneshyari.com/en/article/6528512>

Download Persian Version:

<https://daneshyari.com/article/6528512>

[Daneshyari.com](https://daneshyari.com)